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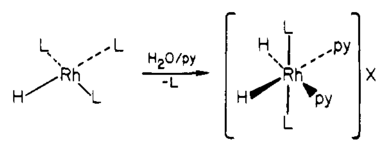
Activation of Water Molecules. 4. Generation of Dihydrogen from Water by Rhodium(I) Hydrido and Rhodium(0) Carbonyl Compounds

Sir:

Previously we reported the oxidative addition of water to monohydridorhodium(I) compounds ligated with electron-donating ligands, e.g., $RhHL_3$ [L = P(i-Pr)$_3$].[1] The product formed in a coordinating solvent like pyridine (py) is the cis-dihydride $[RhH_2(py)_2L_2]OH$ (**1a**), which can be isolated as its BPh_4 salt



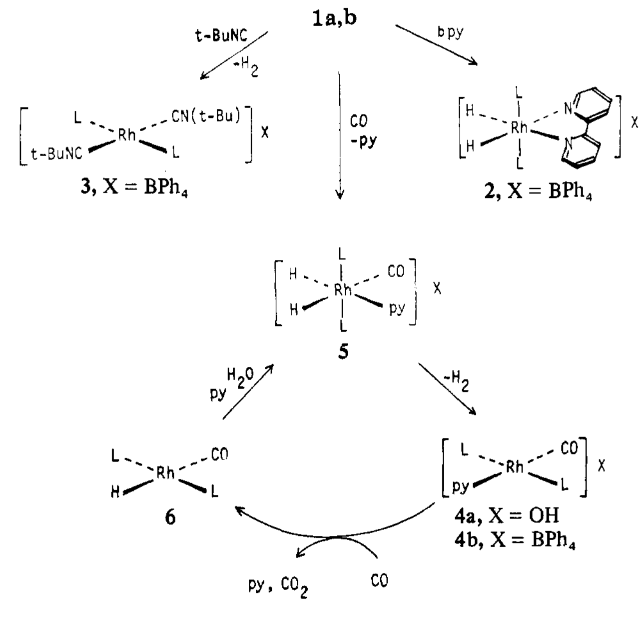
1a, X = OH
1b, X = BPh_4

(**1b**). In spite of its cis ligation, the Rh–H bonds in **1b** were found to be rather thermally stable, in contrast to $[RhH_2(S)_2(PPh_3)_2]^+$ (S = solvent) which dissociates H_2 in vacuo.[2a] When **1a** is heated (90 °C, in dioxane), it merely decomposes into an untractable oil, and irradiation (low-pressure Hg lamp) fails to give any perceptible production of dihydrogen. Our concern then was to produce dihydrogen by utilizing $RhHL_3$ via oxidative addition of water. However, the PPh_3 analogue, $RhH(PPh_3)_3$, which lacks sufficient nucleophilic character to undergo oxidative addition of water, cannot be a candidate for the purpose.

In the absence of systematic information on ligand effects on the Rh–H bond strength in cis-dihydrido compounds of type **1**, we investigated the effect of replacing the equatorial pyridine ligands with other ligands. First, 2,2′-bipyridine (bpy) was examined to see the chelating effect. The reaction of **1b** with bpy (room temperature, in THF) gave $\{RhH_2(bpy)[P(i\text{-}Pr)_3]_2\}BPh_4$[3] (**2**) (Scheme I). The cis-dihydrido ligation in **2** is readily established by its IR [ν(Rh–H) 2080, 2135 cm^{-1}] and ^{1}H NMR [−17.2 (q, Rh–H, $J_{H\text{-}P} = J_{H\text{-}Rh}$ = 15.6 Hz), 1.02 (q, CH_3, $^3J_{H\text{-}P} + {}^5J_{H\text{-}P}$ = 12.0 Hz, $J_{H\text{-}H}$ = 6.0 Hz)] data. **2** is somewhat more stable than **1b**, and no dihydrogen evolution is observed upon heating at 90 °C for 10 h in aqueous dioxane, **2** being recovered quantitatively.

Facile dihydrogen evolution from **1b** takes place by treatment with t-BuNC. Thus, on addition of t-BuNC to a THF solution of **1b** at room temperature, dihydrogen evolution commenced instantaneously with effervescence and was completed within a few minutes. From the solution, *trans*-$\{Rh(t\text{-}BuNC)_2[P(i\text{-}Pr)_3]_2\}BPh_4$[4] (**3**) was isolated as golden yellow crystals (80%). Brisk dihydrogen evolution also occurred on introduction of CO

Scheme I



into a THF solution of **1b** under ambient conditions, *trans*-$\{Rh(CO)(py)[P(i\text{-}Pr)_3]_2\}BPh_4$[5] (**4b**) being produced (80%). The formation of **4b** from **1b** probably involves an intermediate **5**[6] (see Scheme I). These results suggest that electron-donating ligands like pyridine and dipy stabilize the dihydrido coordination in **1a,b** whereas electron-withdrawing t-BuNC and CO reduce the bond strength.[7] Higher Rh–H stretching frequencies are observed for cis-dihydridobicarbonato, and -formato complexes, $RhH_2(B)L_2$ (B = HCO_3, ν(Rh–H) 2120, 2140 cm^{-1}; B = HCO_2, ν(Rh–H) 2130, 2145 cm^{-1}).[8] Consistent with these Rh–H stretching frequencies, these compounds do not generate dihydrogen at ambient temperature even in high vacuum.

A hydridocarbonyl compound, *trans*-$[RhH(CO)L_2]$ [**6**, L = P(i-Pr)$_3$],[9] prepared as yellow crystals by treating $RhHL_3$ [L = P(i-Pr)$_3$] with methanol at room temperature, undergoes oxidative addition of water, producing H_2 (70%) and *trans*-$\{Rh(CO)(py)[P(i\text{-}Pr)_3]_2\}OH$ (**4a**); the latter was isolated as **4b** (55%). Initial formation of the water adduct **5** must be postulated to account for the dihydrogen generation. Therefore, it is most likely, also reasonable, that the same intermediate **5** is involved for the two routes, **1b** → **4b** and **6** → **4a**.

An attempt to prepare **6** through a direct reaction of $RhHL_3$ [L = P(i-Pr)$_3$] with CO in n-hexane at ambient temperature failed. Unexpectedly, the product obtained was a binuclear Rh(0) carbonyl compound, $Rh_2(CO)_3L_3$ (**7**), as red crystals. The formulation of **7** is based on the elemental analysis, IR, and ^{1}H NMR data,[10] no indication being obtained for the presence of hydride ligands. The formation apparently proceeds via $[Rh(CO)_3L]_2$

(1) Yoshida, T.; Okano, T.; Saito, K.; Otsuka, S. *Inorg. Chim. Acta* **1980**, *44*, L135–L136.

(2) (a) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 1397–1401. (b) *Ibid.* **1976**, *98*, 2134–2143.

(3) Analytical sample obtained from THF–toluene contains 1 mol of toluene. Anal. Calcd for $C_{59}H_{80}N_2P_2BRh$: C, 71.36; H, 8.12; N, 2.82. Found: C, 71.01; H, 7.84; N, 2.92.

(4) Anal. Calcd for $C_{52}H_{80}N_2P_2BRh$: C, 68.92; H, 8.86; N, 2.87. Found: C, 68.77; H, 8.86; N, 3.08. IR (Nujol), ν(C≡N) 2115 cm^{-1}; ^{1}H NMR (acetone-d_6) 1.49 (s, t-Bu), 1.38 (q, CH_3, $^3J_{H\text{-}P} + {}^5J_{H\text{-}P}$ = 13.2 Hz, $J_{H\text{-}H}$ = 6.6 Hz), ~2.3 (m, CH).

(5) Analytical sample recrystallized from THF–toluene contains 2 mol of toluene. Anal. Calcd for $C_{62}H_{83}NOP_2BRh$: C, 72.01; H, 8.09; N, 1.35. Found: C, 72.03; H, 8.05; N, 1.43. IR (Nujol), ν(CO) 1985 cm^{-1}; ^{1}H NMR (THF-d_8) 1.25 (q, CH_3, $^3J_{H\text{-}P} + {}^5J_{H\text{-}P}$ = 13.0 Hz, $J_{H\text{-}H}$ = 6.5 Hz), ~1.9 (m, CH).

(6) Indirect support is a similar reaction of $[RhH_2(PEt_3)_3]OH$, a water adduct of $RhH(PEt_3)_3$, with CO which gives a hexacoordinate cis dihydride, $[RhH_2(CO)(PEt_3)_3]^+$. However, instead of **5**, a possibility of forming a nonsolvated pentacoordinate cis-dihydrido complex, $\{RhH_2(CO)[P(i\text{-}Pr)_3]_2\}^+$, could not be excluded.

(7) $[RhH_2(S)_2(PPh_3)_2]^+$ with CO is known to give $[Rh(CO)(S)(PPh_3)_2]^+$ while the reaction with $AsMe_2Ph$ or dipy gave $[RhH_2(PPh_3)_2L_2]^+$ (L = $AsMe_2Ph$ or L_2 = dipy).[2]

(8) Yoshida, T.; Thorn, D. L.; Okano, T.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 4212–4221.

(9) Anal. Calcd for $C_{19}H_{43}OP_2Rh$: C, 50.44; H, 9.58. Found: C, 50.49; H, 9.65. IR (Nujol), ν(Rh–H) 1980 cm^{-1}; ν(CO) 1920, 1942 cm^{-1}; ^{1}H NMR (benzene-d_6) −5.9 (dt, Rh–H, $J_{H\text{-}Rh}$ = 14.3 Hz, $J_{H\text{-}P}$ = 20.0 Hz), 1.23 (q, CH_3, $^3J_{H\text{-}P} + {}^5J_{H\text{-}P}$ = 13.8 Hz, $J_{H\text{-}H}$ = 6.9 Hz), ~2.0 (m, CH).

(10) Anal. Calcd for $C_{30}H_{63}O_3P_3Rh_2$: C, 46.57; H, 8.34. Found: C, 46.48; H, 8.19. IR (Nujol), ν(CO) 1732, 1768, 1957 cm^{-1}; ^{1}H NMR (benzene-d_6) ~1.0 (m, CH_3), ~1.8 (m, CH).

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(**8**),[11] which was isolated as orange-yellow crystals from the re-

$$\mathrm{RhHL_3} \xrightarrow[-\mathrm{L}]{\mathrm{CO}} \textit{trans}\text{-}\underset{\mathbf{6}}{\mathrm{RhH(CO)L_2}} \xrightarrow[-\mathrm{H_2},-\mathrm{L}]{\mathrm{CO}} \underset{\mathbf{8}}{[\mathrm{Rh(CO)_3L}]_2} \xrightarrow[\text{under } \mathrm{N_2}]{\mathrm{L},-\mathrm{CO}} \underset{\mathbf{7}}{\mathrm{Rh_2(CO)_3L_3}}$$

action of $RhHL_3$ and CO. **8** is extremely unstable in the absence of CO. Thus, when the CO atmosphere of the flask containing the *n*-hexane solution of **8** was replaced with dinitrogen, **7** was obtained in a low yield (18%). The yield (from **8**) was much improved by adding free L [P(*i*-Pr)$_3$] to the reaction. It was confirmed that **8** and **7** are also formed from the reaction of CO with **6** separately prepared.[12]

It is of interest to note that the carbonylrhodium(0) compound **7** reacts with water, producing H_2. Thus, a red solution of **7** in pyridine containing 1 mol of free P(*i*-Pr)$_3$ turned pale yellow immediately on addition of water at room temperature with H_2 evolution (50% based on **7**). From the solution was isolated **4b** (68%) by adding $NaBPh_4$. The capability of rhodium carbonyl compounds to undergo facile oxidative addition of water is remarkable in view of the presence of electron-withdrawing CO ligands. The formation of the Rh(I) compound **4a** is also interesting, since **4a** reacts with CO to give CO_2 and **6**, thus suggesting the possibility of catalyzing the water–gas shift reaction. Indeed, we discovered that $RhHL_3$ compounds and related species such as **1**, **6**, **4a**, and **7**, etc. serve as active catalysts. The details will be described separately.[13]

Transition-metal compounds would provide a low-energy system for the catalytic photodissociation of water, which is one of the intensive current research interests.[14] Although a Rh(I) dimer, tetrakis(1,3-diisocyanopropane)dirhodium(2+),[15] was proposed as such a system, hydrogen evolution remains stoichiometric. Therefore, the present study should contribute to our fundamental knowledge for the water-splitting systems.

(11) Anal. Calcd for $C_{24}H_{42}O_6P_2Rh_2$: C, 41.40; H, 6.37. Found: C, 41.61; H, 6.28. IR (Nujol), ν(CO) ~1950 cm^{-1}; ^{1}H NMR (benzene-d_6 under CO) 0.9 (br, CH_3), ~1.6 (br, CH).

(12) A similar formation of rhodium(0) carbonyl compounds [Rh(CO)$_2$L$_2$]$_2$ and [Rh(S)(CO)L$_2$]$_2$ (S = solvent) from a hydrido complex RhH(CO)L$_3$ (L = PPh$_3$) was reported: Evans, D.; Yagupsky, G.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 2660–2665.

(13) Yoshida, T.; Okano, T.; Otsuka, S., to be published.

(14) Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F.; Gleria, M. *Science (Washington D.C.)* **1975**, *189*, 852–856.

(15) Mann, K. M.; Lewis, L. S.; Miskowski, V. M.; Erwin, D. K.; Hammond, G. S.; Gray, H. B. *J. Am. Chem. Soc.* **1977**, *99*, 5525–5526. Miskowski, V. M.; Sigal, I. S.; Mann, K. R.; Gray, H. B.; Milder, S. J.; Hammond, G. S.; Rayson, P. R. *Ibid.* **1979**, *101*, 4383–4385.

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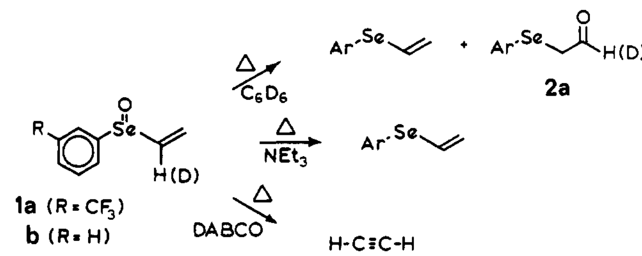
Organoselenium Chemistry. Formation of Acetylenes and Allenes by Syn Elimination of Vinyl Selenoxides[1]

Sir:

The syn elimination of alkyl selenoxides to give olefins is one of the most important applications of selenium in organic synthesis.[2] We report here that under the proper conditions this reaction also takes place with vinyl selenoxides to give acetylenes and, in certain situations, allenes.

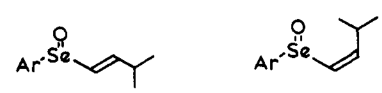
Thermolysis of *m*-trifluoromethylphenyl vinyl selenoxide[3] (**1a**) in benzene forms no acetylene. The products are variable amounts of the reduced selenide and arylselenoacetaldehyde **2a**. The latter



is presumably formed by reaction of vinyl selenide or vinyl selenoxide with selenenic acid.[5] An alternative mechanism involving addition of ArSeOH to acetylene[1b] was ruled out when it was found that deuterated **1a** gave **2a** with deuterium only at the aldehyde position. If the thermolysis of **1a** is carried out with triethylamine present, the formation of **2a** is completely suppressed, but reduction is still the major process. On the basis of the theory that triethylamine is now the reductant, other amines not as easily oxidized to immonium cations were tried. These included 1,4-diazabicyclo[2.2.2]octane (Dabco), quinuclidine, and hexamethyldisilazane. In the presence of 1–2 equiv of these amines, vinyl selenoxides are smoothly thermolyzed to acetylenes at 95 °C. Of the amines used, Dabco is most effective in preventing both selenenic acid addition and reduction. A pericyclic syn elimination mechanism for the acetylene formation is consistent with all of the experimental results:

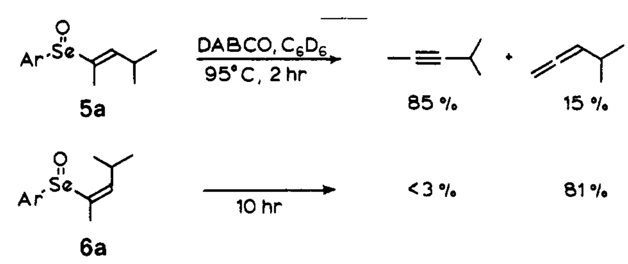
(1) The rate of elimination of **1a** is the same when 0.5, 2.9, or 5.1 equiv of Dabco are present. The reaction, thus, is not an E2 elimination.

(2) The selenoxides **3a** and **4a**[1c,3] show very different behavior. Compound **3a** gives a 63% (by NMR) yield of 3-methylbutyne in 20 h at 95 °C whereas **4a** gives only a trace (<5%) of acetylene after 60 h, together with about 50% of reduced selenide.



3a **4a**

(3) Compounds **5a** and **6a**[3] were thermolyzed at 95 °C, with the results shown below. The (*Z*)-selenoxide **6a**, which cannot undergo syn elimination to an acetylene like the *E* isomer **5a**, reacts more slowly and gives predominantly allene.



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(2) For recent reviews see: (a) H. J. Reich in "Oxidation in Organic Chemistry. Part C", W. Trahanovsky, Ed., Academic Press, New York, 1978, p 1; (b) H. J. Reich, *Acc. Chem. Res.*, **12**, 22 (1979); (c) D. L. J. Clive, *Tetrahedron*, **34**, 1049 (1978).

(3) Selenoxides were prepared by oxidation with *m*-chloroperoxybenzoic acid[4] in dichloromethane. Compounds in the **a** series have Ar = *m*-$CF_3C_6H_4$ whereas those in the **b** series have Ar = C_6H_5.

(4) M. Sevrin, W. Dumont, and A. Krief, *Tetrahedron Lett.*, 3835 (1977). These authors also observed that vinyl selenoxides give selenides on thermolysis.

(5) The reaction of olefins with PhSeOH is a common side reaction during selenoxide syn eliminations.[1a,6] It can usually be prevented by carrying out the elimination in the presence of alkylamines.[1a]

(6) T. Hori and K. B. Sharpless, *J. Org. Chem.*, **43**, 1689 (1978).

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